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Activation of Carbon Dioxide by New Mixed Sandwich Uranium(III) Complexes  
Incorporating Cyclooctatetraenyl and Pyrrolide, Phospholide, or Arsolide Ligands

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**Electronic Supplementary Information**

## Cyclic voltammetry

Studies were conducted in an MBraun glovebox under argon using a BASi Epsilon-EC potentiostat under computer control. *iR* drop was compensated for by using the feedback method. All experiments were conducted using a gold disc (2.0 mm<sup>2</sup>) or glassy carbon disc (7.0 mm<sup>2</sup>) working electrode, platinum wire counter electrode and silver wire pseudo-reference electrode. Ferrocene (*ca.* 1 mg) was added to all solutions after initial voltammograms had been obtained to obtain the [FeCp<sub>2</sub>]<sup>+0</sup> reference couple. Samples were prepared by dissolving the analyte (5 – 10 mM) in a solution of supporting electrolyte (5 mM [<sup>n</sup>Bu<sub>4</sub>N][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) in 1 ml THF). Studies of **1** showed five electrochemical events, of which four were stable over 5 cycles. The fifth event at -0.05 V *vs* FeCp<sub>2</sub><sup>+0</sup> diminished with successive scans. Studies of **2** showed two quasi-reversible waves (process 3 and 4) and one distorted wave, all of which were stable over a minimum of four cycles. Complex **3** exhibited three distorted waves, which were also stable over several cycles. Distortion of the waves prevented determination of E<sub>1/2</sub> for some processes. All reported potentials are referenced to the FeCp<sub>2</sub><sup>+0</sup> redox couple, which was measured by addition of ferrocene (*ca.* 1 mg) to the solution after all initial voltammograms had been obtained.

Compound	Process 1 E <sub>1/2</sub> /V	Process 2 E <sub>1/2</sub> /V	Process 3 E <sub>1/2</sub> /V	Process 4 E <sub>1/2</sub> /V	Process 5 E <sub>1/2</sub> /V
<b>1</b>	-2.50	-1.88	-1.42	-0.62	-0.05
<b>2</b>		-1.92 <sup>a</sup>	-1.32	-0.81	
<b>3</b>		-1.89 <sup>a</sup>	-1.26 <sup>b</sup>	-0.71 <sup>b</sup>	

Table S1 Electrode potentials *vs* FeCp<sub>2</sub><sup>+0</sup> in 0.05 M [<sup>n</sup>Bu<sub>4</sub>N][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/THF at 100 mV·s<sup>-1</sup>.

<sup>a</sup>E<sub>p</sub><sub>c</sub> values given instead of E<sub>1/2</sub>; <sup>b</sup>E<sub>p</sub><sub>a</sub> values given instead of E<sub>1/2</sub>.

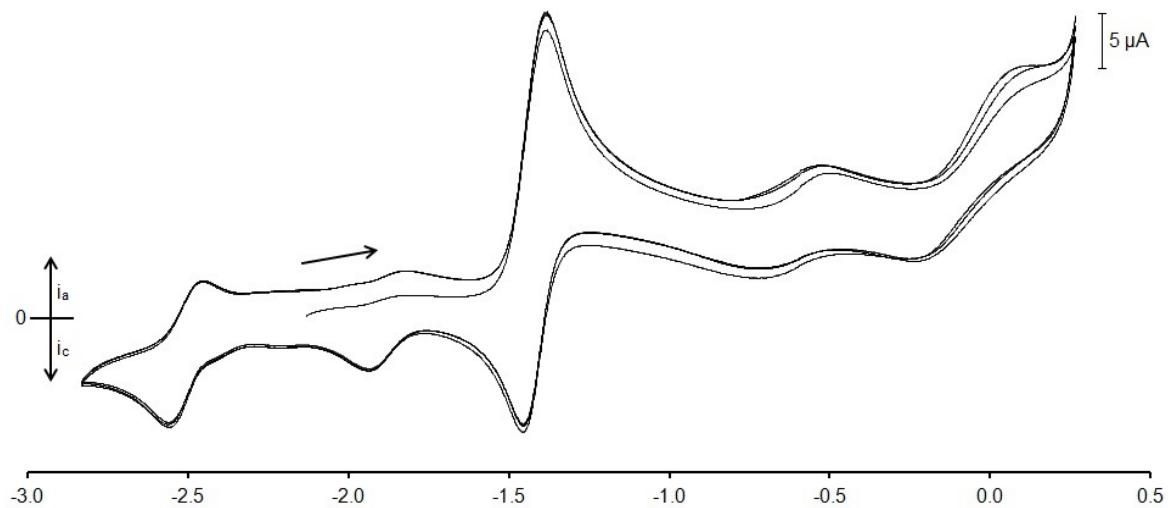


Figure S1: Overlaid CV scans (3 cycles) of  $[\text{U}(\text{COT}^{\text{TIPS}2})(\text{Cp}^{\text{NMe}4})]$  (1) in 0.05 M  $[^n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ /THF at  $100 \text{ mV}\cdot\text{s}^{-1}$ .

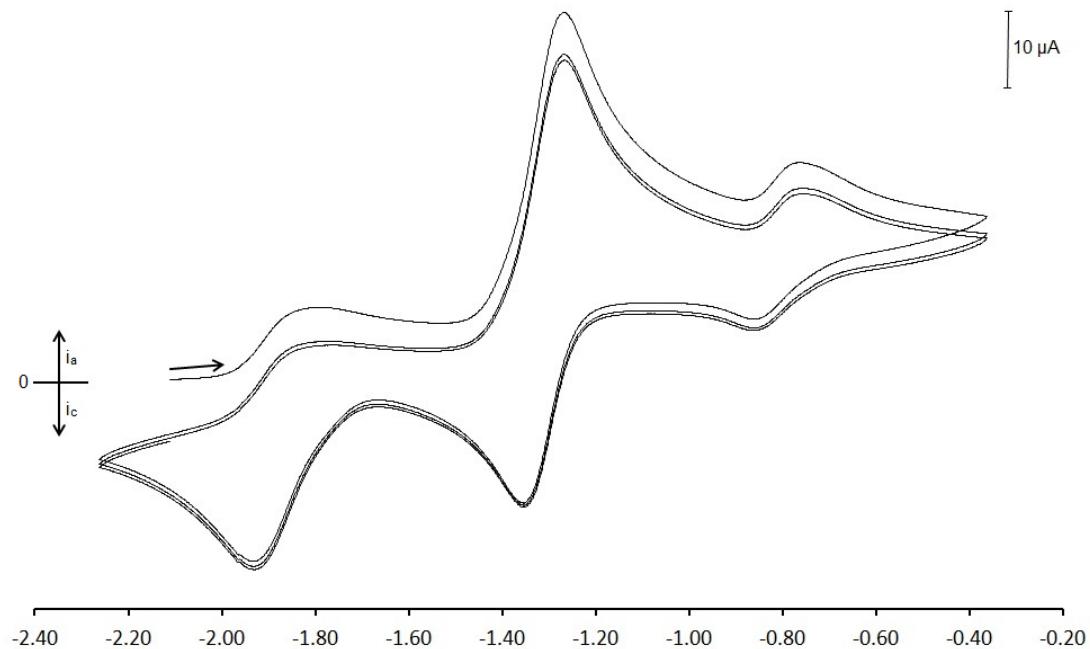


Figure S2: Overlaid CV scans (3 cycles) of  $[\text{U}(\text{COT}^{\text{TIPS}2})(\text{Cp}^{\text{PMe}4})]$  (2) in 0.05 M  $[^n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ /THF at  $100 \text{ mV}\cdot\text{s}^{-1}$ .

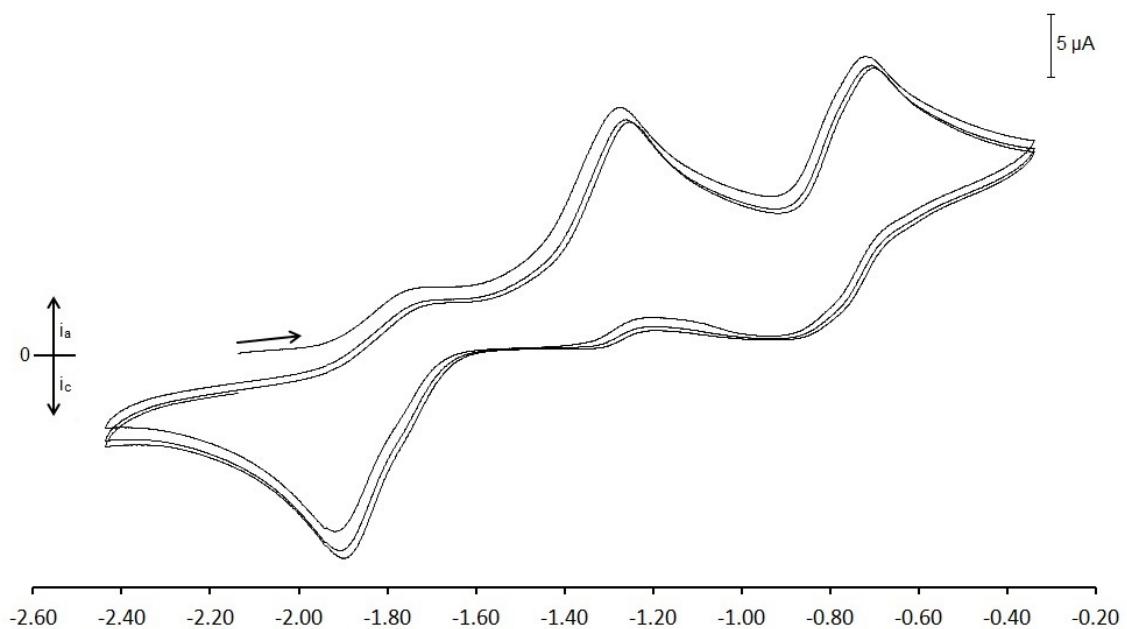


Figure S3: Overlaid CV scans (3 cycles) of  $[\text{U}(\text{COT}^{\text{TIPS}2})(\text{Cp}^{\text{AsMe}4})]$  (3) in 0.05 M  $[\text{nBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ /THF at  $100 \text{ mV}\cdot\text{s}^{-1}$ .

### X-ray Crystallographic Studies

Data for **1**, **2**, **3** and **5** were collected on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K  $\alpha$  radiation ( $\lambda = 0.71073$ ) source, and data for **1**·THF were collected using a Agilent Technologies Xcalibur Gemini ultra diffractormer with a Cu K  $\alpha$  radiation ( $\lambda = 1.54184$ ) source at 173 K using an Oxford Cryosystems Cobra low temperature device, operating in  $\omega$  scanning mode with  $\Psi$  and  $\omega$  scans to fill the Ewald sphere. The programs used for control and integration were Collect,<sup>1</sup> Scalepack and Denzo.<sup>2</sup> Absorption corrections were based on equivalent reflections using SADABS.<sup>3</sup> Data for **4** were collected and processed by the UK National Crystallography Service at the University of Southampton. The crystals were mounted on a glass fibre with silicon grease, from dried vacuum oil kept over 4 Å molecular sieves in an MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX<sup>4</sup> or Olex2<sup>5</sup> packages and software therein. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were refined using a riding model. Complex **1** could not be collected at high resolution, and the structure only illustrates connectivity. **2** and **3** exhibit disorder of the five-membered ring over two positions. This has been modelled in **2** to illustrate the two positions and has been modelled in **3** by keeping one of the ring carbon atoms isotropic. **4** crystallises with several molecules of hexane in the unit cell which has been modelled using the

SQUEEZE<sup>6</sup> function in PLATION.<sup>7</sup> Several atoms have been made isotropic due to positional disorder within the *iso*-propyl groups. Structural and refinement details are presented in the following tables.

Compound	<b>1</b>	<b>1·THF</b>	<b>2·THF</b>	<b>3·THF</b>
Colour, Habit	Purple, Needle	Brown, Needle	Purple, Needle	Brown Rod
Size /mm	0.10 x 0.12 x 0.18	0.02 x 0.04 x 0.10	0.06 x 0.12 x 0.62	0.04 x 0.06 x 0.18
Empirical Formula	<chem>C68H120N2Si4U2</chem>	<chem>C38H68NOSi2U</chem>	<chem>C38H68OPSi2U</chem>	<chem>C38H68OAsSi2U</chem>
<b>M</b>	1554.09	849.14	866.10	910.05
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	Pbc21	P21/n	P21/n	P21/n
<i>a</i> /Å	12.5424(1)	11.8517(2)	11.8847(7)	11.9699(2)
<i>b</i> /Å	22.7691(3)	14.9317(2)	14.9475(8)	14.9384(2)
<i>c</i> /Å	24.9695(2)	22.2479(3)	22.5236(14)	22.3339(4)
$\alpha$ /°	90	90	90	90
$\beta$ /°	90	91.366(2)	89.568(5)	90.5380(10)
$\gamma$ /°	90	90	90	90
<i>V</i> /Å <sup>3</sup>	7130.77(12)	3936.00(10)	4001.1(4)	3993.36(11)
<i>Z</i>	8	4	4	4
$\mu$ /mm <sup>-1</sup>	4.641	12.386	4.183	4.973
T (K)	173.15	173.15	173.15	173.15
θmin/max	1.62, 27.48	3.565, 61.153	3.429, 29.374	1.64, 27.47
Completeness	0.999, 27.48	0.995	0.872, 29.374	0.999
Reflections	96143 / 15976	21216 / 6020	34897 / 9625	53555 / 9140
Total/Independent				
Rint	0.0649	0.0504	0.0460	0.0843
Final R1 and wR2	0.0333, 0.0765	0.0539, 0.1539	0.0291, 0.0613	0.0396, 0.1146
Largest peak hole/ e. Å <sup>-3</sup>	0.873 / -1.900	6.613 / -2.035	1.03 / -0.97	1.297 / -2.231
ρcalc/g.cm <sup>-3</sup>	1.448	1.433	1.438	1.514

Compound	<b>4</b>	<b>5</b>
Colour, Habit	Orange, Plate	Red Prism
Size /mm	0.01 x 0.06 x 0.07	0.06 x 0.08 x 0.12
Empirical Formula	C <sub>70</sub> H <sub>120</sub> N <sub>2</sub> O <sub>5</sub> Si <sub>4</sub> U <sub>2</sub>	C <sub>70</sub> H <sub>120</sub> O <sub>5</sub> Si <sub>4</sub> P <sub>2</sub> U <sub>2</sub>
M	1658.11	1692.03
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P21/c
a /Å	12.9610(9)	22.3131(4)
b /Å	14.6337(10)	15.0442(3)
c /Å	22.2106(16)	22.7699(4)
α /°	97.035(6)	90
β /°	97.053(6)	96.826(1)
γ /°	102.983(7)	90
V /Å <sup>3</sup>	4024.5(5)	7589.3(2)
Z	2	4
μ /mm <sup>-1</sup>	4.121	4.412
T (K)	173.15	173.15
θmin/max	2.430, 27.562	3.439, 27.492
Completeness	97.7, 27.562	0.988
Reflections	47825 / 18150	53555 / 9140
Total/Independent		
Rint	0.0794	0.0843
Final R1 and wR2	0.0703, 0.1751	0.0550, 0.1586
Largest peak hole/ e. Å <sup>-3</sup>	4.02/-2.64	1.159 / -8.442
ρcalc/g.cm <sup>-3</sup>	1.368	1.514

CCDC 1051779-1051784 contain the supplementary crystallographic data for this paper.

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<sup>7</sup> A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.